Interaction of $\alpha$-TiCl$_3$ with organoaluminium compounds and its correlation with propylene polymerization

I. Kinetics of interaction

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SUMMARY

The interaction between the catalytic components of a Ziegler-Natta sterospecific system formed by TiCl$_3$ and AlEt$_3$ in heptane was studied. The extent of interaction was monitored by following the rate of chlorine exchange between the solid and liquid phase and by the development of gaseous hydrocarbons. The experimental results show that interaction between the catalytic components is a necessary but not the only condition for the formation of active centers of sterospecific polymerization.

INTRODUCTION

Since the discovery of Ziegler-Natta systems the structure of active centers and mechanism of their formation from the catalytic components has been continuously discussed in the literature (1-4). According to Keii et.al. the real active centers of polymerization are formed by an irreversible reaction between monomer and the equilibrium surface complex of titanium trichloride with an organoaluminium component (5). In the present work, an attempt was made to correlate the interaction occurring between the catalytic components and the polymerization process.
EXPERIMENTAL
Chemicals and their purification

N-heptane was first rectified in a column, then treated with sulfuric acid, washed with distilled water and dried with anhydrous Na₂SO₄. The product was subsequently re-distilled with sodium metal and stripped with purified nitrogen before use.

Titanium trichloride was prepared by the reduction of titanium tetrachloride with hydrogen on tungsten spiral and ground under inert atmosphere in an Attritor-type ball mill (6). Triethylaluminium, diethylaluminium chloride and ethylaluminium dichloride were purified by vacuum rectification and stored in n-heptane solution. Propylene used after rectification had the following composition: 99.88% C₃H₆; 0.11% C₃H₈.

Apparatus and Procedure

The interaction of the catalytic components was carried out in a stirred 300 ml glass reactor joined to a high-vacuum line through a ground joint (7). While the interaction was underway, samples of the gas phase were taken out and analysed by gas chromatography. Methane, ethane and ethyl were separated using a 1m column packed with alumino-silicate while the hydrocarbons were analysed on a 9m column packed with 20% di-(2-ethylhexyl)phthalate on Chromosorb W. A flame ionisation detector was used in both cases. For hydrogen, an Alusil-packed column was employed in combination with a thermal conductivity detector.

Further analysis was carried out to find out the composition of the solid phase remaining after the interaction. For this, the liquid phase was removed by centrifuging the slurry and the remaining solids were dried in a vacuum oven. Titanium, chlorine, carbon and hydrogen contents were determined by elemental analysis.

RESULTS AND DISCUSSION

The kinetic study of interaction reactions is based on following degree of conversion of the exchange and decomposition reactions (1,2). The portion of chlorine found in the liquid phase, called $c_{cl}$, is expressed in % of total Cl originally present in TiCl₃; the degree of